Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater

Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater

K.E. Dobbie[1, 2], K.V. Heal[1]*, J. Aumônier[3], K.A Smith[1], A. Johnston[4] and P.L. Younger[3]

[1]*School of GeoSciences, The University of Edinburgh, Crew Building, West Mains Road, Edinburgh, EH9 3JN, UK*

[2]*Current affiliation: SEPA, Heriot Watt Research Park, Avenue North, Edinburgh, EH14 4AP, UK*

[3]*Institute for Research on Environment and Sustainability, University of Newcastle, Devonshire Building, Newcastle upon Tyne, NE1 7RU, UK*

[4]*Scottish Water, Galafoot Office, Winston Road, Galashiels, TD1 3HH, UK*

* Corresponding author. Tel: +44 131 650 5420; fax: +44 131 662 0478

E-mail address: k.heal@ed.ac.uk

Abstract

Treatment of polluting discharges from abandoned coal mines in the UK currently produces ca 30,000 t y^{-1} of hydrous iron oxides ("ochre"), for which there is no major end-use, but which has previously been shown to have potential for removing P from wastewater and agricultural runoff. The efficiency of ochre for P removal from wastewater was investigated in experiments at two sites in the UK: Leitholm in Scotland and Windlestone in England. The three-year experiment at Leitholm involved diverting secondary-treated wastewater effluent through a trough which contained granular and pelletized ochre at different times. In the nine-month experiment at Windlestone, beds of ochre pellets in horizontal and vertical flow configurations were tested. The ochre treatment systems at Leitholm reduced influent concentrations of total P (TP) and TP mass by ca 80 and ca 50%, respectively, during optimal flow conditions, and achieved a removal rate of up to 65±48 mg TP kg^{-1} ochre d^{-1}. There was no detectable release of potentially toxic metals from the ochre during the experiments. P removal rates by concentration were inversely related to flow and declined during the different phases of the experiments, probably due to clogging. At Windlestone, higher removal rates up to 195 mg TP kg^{-1} ochre d^{-1} were achieved for short periods of time following cleaning of the experimental system. Ochre has considerable potential to remove P from wastewater in a multi-stage treatment system and has a lifetime estimated to be 10 times longer than other substrates tested for P removal.

Keywords: Field experiment; Mass removal; Operational lifetime; Potentially toxic metals; Waste recycling; Wastewater treatment

1. Introduction

Fe(II) in water draining from disused coal mines readily oxidises to Fe(III) and precipitates as coatings on stream beds that may smother aquatic life (Younger et al., 2002). Thus treatment involves oxidation of the Fe(II) and precipitation as "ochre" ($(Fe(OH)_3$ and FeO(OH)). At present in the UK, after dewatering the ochre is landfilled at a total disposal cost of ca £80-100 t^{-1} (Morritt, A., personal communication). However, ochre has potential for combatting another threat to aquatic ecosystems, i.e. P in effluent from wastewater treatment plants (WWTPs) and agricultural runoff, which contributes to eutrophication (Mainstone and Parr, 2002). Controls on P discharges from WWTPs (EC, 1991) are currently mainly achieved in the UK by costly dosing with chemicals, e.g. Fe(III) salts.

Short-term laboratory experiments have demonstrated P removal from wastewater by various iron-rich substrates (reviewed by Johansson Westholm, 2006). Batch experiments and a nine-month trough experiment with ochre proved particularly effective (Heal et al., 2004a), with the measured uptake of > 20 g P kg dry $ochre^{-1}$ being an order of magnitude higher than that of other materials tested. In previous publications (Heal et al., 2003; Heal et al., 2004b; Sibrell, 2007) a number of potential applications are described of ochre for P removal from agricultural runoff and wastewater. Here we report the results of field experiments set up to evaluate how ochre performs at a more realistic scale, investigating long-term P removal from wastewater and also any associated release of potentially toxic metals that might have adsorbed onto the ochre during mine water treatment.

2. Materials and methods

2.1 Leitholm experiment

The principal experiment was conducted at the WWTP at Leitholm, south-east Scotland, UK (55.69^{o} N, 2.34^{o} W), which treats 150 population equivalents of sewage d^{-1} and road runoff. Wastewater receives primary and secondary treatment in a settlement tank and a biological filter. Then it passes into a horizontal subsurface flow wetland (175 m^2 area planted with common reed (*Phragmites australis*) in 0.5-0.6 m deep gravel) for tertiary treatment before entering a settlement tank which discharges into the receiving watercourse. The effluent is dosed with Fe(III) sulphate to ensure compliance with the discharge consent. For the experiment, the outflow from the biological filter was transferred by a level-activated pump to an ochre-filled galvanised steel trough (2.1 m^3 capacity, Fig. 1) located before the wetland. The wastewater was dispersed along the trough via a perforated 0.11 m diameter pipe and flowed up through the ochre, spilling out over the trough rear wall into the wetland.

FIG 1

Two different forms of ochre were used in the experiment:

(1) Coarse granular ochre from drying beds at the mine water treatment plant at Polkemmet, central Scotland, with a saturated hydraulic conductivity of 26-32 m d^{-1} and an inter-clastic porosity of 30%. The ochre was shown by x-ray diffraction to consist predominantly of goethite (FeO(OH)) and its composition by % dry weight was Fe 65, Ca 7.0, Al 0.7 and Mg 0.6 (Heal et al., 2004a).

(2) Near-spherical ochre pellets (6.4–9.5 mm diameter), made from dried ochre from treatment plants at Polkemmet and Acomb, northern England, to create a material that was robust and easy to handle but which retained its reactivity. The pellets were made by mixing oven-dried and sieved ochre with Portland cement, a surfactant and water, agglomerating the mixture in a pan pelletizer and then drying at 105 °C. The pellets thus formed had a higher hydraulic conductivity (22×10^3 m d^{-1}) than unpelletized ochre and an inter-clastic porosity of 35%.

Monitoring of the wetland began in July 2002, the trough was introduced in November 2003, and the experiment continued until January 2006. Rainfall and wetland water depth were measured hourly from July 2002 until December 2004, using an ARG 100 tipping bucket rain gauge (Environmental Measurements Ltd, Sunderland, UK) and a PDCR1830 pressure transducer (Druck, Leicester, UK), connected to a CR10X datalogger (Campbell Scientific Inc, Logan, UT, USA). Flow from the biological filter was measured from January 2003 until January 2006 at 15-min intervals using a Xytec 7050 IS survey meter (Buhler Montec, Dusseldorf, Germany). At 1-4 wk intervals the outflows from the biological filter, wetland and the trough (after installation) were sampled and analysed in Scottish Water laboratories for total P (TP), soluble reactive P (SRP) and total and dissolved (0.45 μm membrane-filtered) metals (Al, Cd, Cr, Cu, Fe, Ni, Pb, Zn). TP (limit of detection (LOD) 0.02 mg L^{-1}) was determined colorimetrically (molybdate method) after UV digestion, using a Skalar SAN System auto-analyser (Breda, The Netherlands). SRP was similarly determined (LOD 0.02 mg L^{-1}) after 0.45 μm membrane-filtration, using a

Kone auto-analyser (Espoo, Finland). The metallic elements were determined with a PerkinElmer Optima DV3300 ICP-OES instrument (Wellesley, MA, USA).

The experiment compared P removal from wastewater with and without ochre present and the effectiveness of ochre in granular and pellet form and had four phases, described below. Phase 1 (July 2002 – October 2003) established the efficiency of P removal in the wetland in the absence of ochre. From July 2002 to June 2003 (Phase 1a) the wetland had a relatively stable water depth of 26.0±0.1 cm. Then, failure of the water level control mechanism resulted in mainly subsurface water flow in the wetland and shallower water depths in Phase 1b and thereafter, with flooding only occurring briefly after heavy rain. After Phase 1b the trough was installed which contained granular ochre during Phase 2 (November 2003 – March 2005). Uneven flow occurred at first (Phase 2a), with outflow occurring along only a short section of the trough wall, which was overcome by introducing a coarse gravel layer below the ochre (Fig. 1) in February 2004. This arrangement was maintained (Phase 2b) until March 2005. Mean water residence time in the trough was determined in July 2004 using fluorescent rhodamine WT dye and a 10-005 fluorimeter (Turner Designs Inc., Sunnyvale, CA, USA). In Phase 3 (May – September 2005), the granular ochre was replaced with ochre pellets. The inflow was restricted to 0.05 L s^{-1} in Phase 4 (November 2005 – January 2006) and the ochre pellets in half the length of the trough were also replaced. The number of datapoints in each phase was 22 (17 in Phase 1a, 5 in Phase 1b), 27, 6 and 8, respectively, after rejection of two outliers in Phase 2 (Rorabacher, 1991).

2.2 Windlestone experiment

A second experiment was conducted between June 2004 and February 2005 at Windlestone WWTP, north-east England (54.39^{o} N, 1.33^{o} W), to further test P removal by ochre pellets. Final effluent from the WWTP was pumped into one end of a tank and passed by horizontal saturated flow through a ca 0.15 m wide band of 20-25 mm diameter gravel into a bed containing 1166 kg ochre pellets then through a second gravel band, retained by 4 mm mesh, and finally over a weir (Fig. 2a). Preferential flow over the surface was prevented by a solid barrier. The initial inflow rate of 0.75 L s^{-1} was decreased during the experiment to 0.23 and then to 0.21 L s^{-1}. These gave retention times of 7, 23 and 26 min, respectively, for effluent in the tank. The permeability of the ochre bed decreased rapidly due to input of organic and particulate matter necessitating periodical cleaning. The tank was reconfigured for vertical saturated flow conditions from December 2004 to February 2005. A slightly smaller (1027 kg) bed of fresh ochre pellets was installed above layers of gravel and plastic media of high conductivity to avoid preferential flow (Fig. 2b). A constant inflow of 0.21 L s^{-1} wastewater was distributed by spray bars. Despite a filter on the inflow, organic matter accumulated in the spray bars and was removed manually every 7 d. In both configurations tank inflow and outflow samples were collected every 25 h using two automatic samplers, with the outflow sample collected after a time lag equivalent to the retention time of effluent within the tank. Samples were analysed colorimetrically (molybdate method) for TP after digestion with potassium persulphate.

FIG 2A AND 2B

2.3 Data analysis

Statistical analysis was conducted with Minitab v.14 using general linear model analysis of variance followed by Tukey tests. Significance levels are for $P < 0.05$ unless otherwise stated. The effectiveness of P removal by ochre was assessed by calculating the % P removal by concentration/mass (difference between the inflow and outflow concentration/mass expressed as a % of the inflow concentration/mass). At Leitholm, instantaneous P mass fluxes in the filter outflow/trough inflow, trough outflow and wetland outflow were calculated by multiplying the TP or SRP concentration by the flow rate at each point, and integrated to give the cumulative P mass for each phase of the experiment. Regression relationships between TP or SRP concentrations measured in water samples and measured filter outflow/trough inflow rate were used for Phases 1 and 2. In Phases 3 and 4, P masses were calculated using measured TP and SRP concentrations. Uncertainties for the P masses calculated as described above were estimated from 95% confidence intervals (CI) of the P concentrations calculated either by Sigmaplot v.9 (where P concentrations had been estimated from regression relationships) or for the mean measured P concentrations. Fluxes of potentially toxic metals in the Leitholm experiment were not calculated because concentrations were mostly at or below the limit of detection.

3. Results

3.1 Leitholm experiment

Phosphorus concentrations. In Phases 1a and 1b, mean TP and SRP concentrations were not significantly different between the wetland outflow and the inflow (i.e. filter outflow) (Fig. 3). However, in Phase 2 there was a significant decrease in TP concentration between the trough inflow (i.e., filter outflow) and the

wetland outflow, although differences between trough inflow and trough outflow, and trough outflow and wetland outflow, were not significant. A similar trend for SRP in Phase 2 was not significant. In Phase 3, when ochre pellets were introduced, TP and SRP concentrations were decreased by the trough, but not significantly. However, restricting the flow into the trough in Phase 4 resulted in significant decreases in both TP and SRP concentrations in the trough outflow compared to the inflow.

FIG 3

Metal concentrations. There were no significant differences in metal concentrations in the wetland outflow between any of the experimental phases, i.e., before and after the draining of the wetland or before and after introducing ochre in either form to the system. In Phase 2, mean total Al was significantly lower in the wetland outflow than in the trough outflow (0.60±0.09 and 1.77±0.46 mg L^{-1}, respectively). There were no significant differences in concentrations of metals between any of the water sampling points in Phase 3, while in Phase 4, total Fe was significantly higher in the trough outflow than the inflow (0.40±0.11 and 0.12±0.02 mg L^{-1}, respectively), probably due to particulates washed out from the ochre pellets, as dissolved Fe did not show a similar trend. Dissolved Fe, Cd, Cr, Ni and Pb were below the relevant Environmental Quality Standards (EQS) for freshwater (SEPA, 2002) in all samples in all phases of the experiment. Dissolved Cu and dissolved Al were higher than their EQS of 0.01 and 0.025 mg L^{-1}, respectively, although this was not because of addition of ochre, as exceedance occurred throughout the experiment, and there was no significant change in concentrations by passage through the system. Although compliance with the total Zn EQS 1 of 0.075 mg L^{-1} (to protect the most

sensitive aquatic life) could not be assessed because values were always around the LOD (0.085 mg L^{-1}), concentrations were always less than the EQS 2 value of 0.25 mg L^{-1} (to protect less sensitive aquatic life).

Phosphorus removal. Figure 4a shows the effectiveness of the wetland (wetland and trough after Phase 1) and of the trough alone in TP removal. In Phase 1a, the wetland lowered the TP concentration by 33±7% but only by 10±5% in Phase 1b after drainage, probably due to the decrease in water residence time, and less opportunity for P removal by substrate and plants. In Phase 2 overall TP removal was 21±4%, with the granular ochre-containing trough removing 12±3%. TP removals in Phase 3, when ochre pellets were used, were similar: 20±3% overall, with 12±2% removed by the ochre. These results were not unexpected as, although the granular ochre had a slightly higher P saturation capacity than ochre pellets (26 vs. 22 g P kg^{-1}), P removal by the pellets was predicted to be superior because of improved contact with inflowing wastewater. Although TP removal by the overall system increased in Phases 2 and 3 when ochre in either form was added, the improvement was not significant. In Phase 4, after restriction of the trough inflow to 0.05 L s^{-1}, TP removal by the trough increased significantly to 66±6%.

FIG 4

At first in Phase 4, TP removal by concentration was 85%, but decreased over time (Fig. 4b). The similar decrease in Phase 3 was attributed to biofilm growth and organic matter accumulation in the trough clogging the inter-clastic pore spaces and decreasing aeration. However the effect of reducing conditions on P removal is

uncertain: whilst inorganic P associated with Fe(III) compounds may be released (Patrick et al., 1973), conversely, P sorption could increase because of the presence of freshly formed amorphous Fe(II) hydroxides (Patrick and Khalid, 1974). Wholesale release of P from ochre in the trough is unlikely even if reducing conditions develop in the field because the ochre materials have alkaline pH (Heal et al., 2004a; Mayes et al., in press) and relatively high Ca contents, conducive to precipitation of stable Ca phosphates. The decrease in TP removal in Phases 3 and 4 is unlikely to be due to the ochre becoming saturated with P as the overall removal rate was 5.2 and 0.77 g TP kg^{-1} ochre, respectively (see Table 1), well below the measured P saturation capacity.

P removal by mass in the trough in each phase is summarised in Table 1. The patterns for TP and SRP were similar, with TP influxes and removal rates slightly higher than for SRP. Removal improved in Phase 2b after the flow distribution had been enhanced by the introduction of gravel, and the most effective removal of P was in Phase 4 when the inflow was restricted. The P removal by granular ochre of 24 g TP or 21 g SRP kg^{-1} ochre calculated for Phase 2b, assuming that all P removal in the trough was by ochre, was close to the saturation capacity measured in the laboratory (26 g P kg^{-1} ochre).

TABLE 1

Hydraulic conditions and residence time. In contrast, other studies have reported lower P retention capacities in field-scale systems compared to the performance predicted from laboratory experiments. This is partly because P removal capacities estimated from short-term isothermal batch experiments are not representative of

long-term removal processes in larger-scale systems (Arias et al., 2001; Drizo et al., 2002) and also since P removal in field-scale systems is determined by the hydraulic residence time (Brooks et al., 2000), inflow P concentration and inflow regime as well as the P adsorption capacity of the substrate (Drizo et al., 2002). The theoretical total residence time of wastewater in the trough in Phase 2a of the experiment was 26 min, with 15 min in direct contact with the granular ochre. However, a total residence time of only 12 min was measured during this phase by rhodamine dye tracing, indicating that the flow was channellised and that the contact time of wastewater with the ochre was less than that required for effective P removal in laboratory batch shaking experiments (Heal et al., 2005). In addition to residence time, inflow rate also appeared to affect P removal by the trough, since % TP removal by concentration decreased as flow increased in Phases 2 and 3. TP removal decreased from 9±1% to 6±1% and 2±2% mean ± standard error as the inflow rate to the trough increased from 0-1 to 1-2 and 2-4 L s^{-1}, respectively. The most effective TP removal was in Phase 4, when the inflow rate was restricted, and the mean residence time of effluent with the ochre was maximised at 16 min, indicating that controlling the hydraulics is critical for P removal.

3.2 Windlestone experiment

During the experiment, tank inflow TP concentration varied widely between 0.4 and 4.8 mg L^{-1} due to sewage bypassing the treatment works during high rainfall. When the ochre bed was configured for horizontal flow TP removal by concentration was initially high: 73±3 % (n = 6) after manual cleaning of the bed to remove sediment and organic matter. TP removal increased as inflow was decreased: from 69±2 % (n = 4) at 0.75 L s^{-1} to 82±2 % (n = 2) at 0.21-0.23 L s^{-1}. Under vertical flow

conditions TP removal was also high initially at 78% after 25 h operation, but decreased over time, probably due to biofilm development on the ochre pellets, to 20% mean TP removal after 1000 h operation. The maximum rate of P removal measured was 0.2 g P kg^{-1} ochre d^{-1} during the horizontal flow configuration when inflow of 0.75 L s^{-1} contained 4.8 mg TP L^{-1}. In vertical flow conditions 502 g TP was removed after 1000 h operation, equating to removal of 0.49 g TP kg^{-1} ochre.

4. Discussion

The results from the two experiments indicate that further work is required on the design of full-scale ochre-based treatment units to achieve consistent removal of P from wastewater. The optimum configuration is likely to be a multi-stage system, as described by Drizo et al. (1999). This could include a frequently regenerated gravel filter, before the ochre-filled unit, to remove organic material and suspended solids and minimise clogging of the ochre. Alternatively, the ochre could be backwashed to remove solids and biofilm, although this would probably be more expensive. Since the greatest % P removal occurred when inflow was constant and controlled at Windlestone and in Phase 4 at Leitholm, inflow rates to the ochre unit appear to be important, and should be managed to ensure a minimum of 15 min contact time of effluent with the ochre. A further design improvement would be to operate a minimum of two parallel treatment units. This would allow maintenance without disruption to treatment, and operation of the units alternately or passing through pulses of wastewater could increase the overall P removal capacity of the system. Sibrell (2007) showed in small-scale column experiments that, after 80 h pulsed application, > 80% of incoming phosphorus was still removed from simulated wastewater applied to pelletised acid mine drainage sludge whereas P removal ceased

after 15 h continuous wastewater application. The exact mechanisms involved are not known, but Drizo et al. (2002) suggested that new sites for P adsorption could be created during the resting period by, firstly, the transformation of Fe and Al minerals to more amorphous forms due to a decrease in redox potential and, secondly, the movement of Ca and Fe to the material surface as a result of supersaturated conditions created by an increase in pH when the material is drained.

It is normally recommended that estimates of the lifetime of field-scale P removal systems are based on lower sorption capacities than those determined from small-scale batch experiments (Drizo et al., 2002; Johansson Westholm, 2006). Even when using conservative assumptions the operational lifetime of ochre-based systems for P removal is expected to be much greater than other substrates investigated for wastewater treatment. At Leitholm, assuming a P sorption capacity for ochre pellets of 22 g P kg^{-1} and 54% mass removal of the typical TP loading on the trough (17.8 g P d^{-1}), the operational lifetime of the ca 500 kg ochre pellets in the trough in Phases 3 and 4 is 3.1 y before P saturation occurs and replacement is required. By comparison, a slag with a sorption capacity of 1.2 g P kg^{-1} but a greater density (Shilton et al., 2006) operating at 54% P mass removal would have an operational lifetime in the trough of only 107 d. Thus ochre pellets would last around 10 times as long. Whilst the above estimates of the operational lifetime of field-scale ochre-based treatment systems may appear optimistic, it should be noted that the high P sorption capacity of ochre measured in the laboratory was replicated in Phase 2b in the Leitholm field trial. Even if only 10% of the expected P sorption capacity of ochre pellets is achieved in the field (as reported by Arias et al. (2003) in field trials of calcite for P removal

under high loading conditions) the operational lifetime of the ochre at Leitholm would still exceed that of other substrates.

Once the ochre is saturated with P, it could be used as a slow-release P fertiliser with no adverse effects on crop yield or plant and soil quality (Dobbie et al., 2005; Cucarella et al., 2008). This is a sustainable alternative to mining phosphate deposits for fertiliser production and also has the advantage of recycling a material that would otherwise be landfilled.

5. Conclusions

Field testing within WWTPs has shown that ochre in both granular and pelletized forms removes P effectively from wastewater and that there is no mobilisation of potentially toxic metals. Ochre-based treatment units potentially have higher P removal capacities and operational lifetimes than other substrates tested for this purpose but further work is required on their hydraulic design to maximise P removal capacity and lifetime, such as incorporation of a regenerating filter or backwash system. This use of ochre has potentially lower costs than conventional methods, and also has the sustainability advantage of using a by-product of treating coal mine discharges to address another water problem (eutrophication). Furthermore, once the P removal capacity of ochre is exhausted it can be recycled as a slow-release P fertiliser.

6. Acknowledgements

This work was funded by EPSRC Grants GR/R73539/01 and GR/R73522/01 and Enviresearch Ltd. Scottish Water analysed water samples and built the trough at Leitholm. Northumbrian Water provided access and support at Windlestone. The Coal Authority supplied ochre. The fluorimeter was loaned by the Scottish Environment Protection Agency (SEPA) and the flow logger by the Urban Water Technology Centre, University of Abertay Dundee. At The University of Edinburgh Andrew Gray and John Morman provided analytical support and Nicky Greenhorn produced Figs. 1 and 2.

7. References

Arias, C.A., Brix, H., Johansen, N.-H., 2003. Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland equipped with a calcite filter. Water Sci. Technol. 48(5), 51-58.

Arias, C.A., Del Bubba, M., Brix, H., 2001. Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. Water Res. 35, 1159-1168.

Brooks, A.S., Rosenwald, M.N., Geohring, L.D., Lion, L.W., Steenhuis, T.S., 2000. Phosphorus removal by wollastonite: A constructed wetland substrate. Ecol. Eng. 15, 121-132.

Cucarella, T., Zleski, T., Mazurek, R., Renman, G., 2008. Effect of reactive substrates used for the removal of phosphorus from wastewater on the fertility of acid soils. Bioresource Technol. 99, 4308-4314.

Dobbie, K.E., Heal, K.V, Smith, K.A., 2005. Assessing the performance as a fertiliser and the environmental acceptability of phosphorus-saturated ochre. Soil Use Manage. 21, 231-239.

Drizo, A., Comeau, Y., Forget, C., Chapuis, R.P., 2002. Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. Environ. Sci. Technol. 36, 4642-4648.

Drizo, A., Frost, C.A., Grace, J., Smith, K.A., 1999. Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. Water Res. 33, 3595-3602.

EC, 1991. Directive 91/271/EEC concerning urban wastewater treatment. Official Journal of the European Communities L135, 40-52 (21.05.91).

Heal, K.V., Younger, P.L., Smith, K.A., Glendinning, S., Quinn, P., Dobbie, K.E., 2003. Novel use of ochre from mine water treatment plants to reduce point and diffuse phosphorus pollution. Land Contam. Reclam. 11, 145-152.

Heal, K.V., Younger, P.L., Smith, K.A., McHaffie, H., Batty, L.C., 2004a. Removing phosphorus from sewage effluent and agricultural runoff using recovered ochre. In:

Valsami-Jones, E. (Ed.). Phosphorus in Environmental Technology: Removal, Recovery and Applications. IWA Publishing, London, pp. 320-334.

Heal, K.V., Younger, P.L., Smith, K.A., Quinn, P., Glendinning, S., Aumônier, J., Dobbie, K.E., McHaffie, H., Dimoliatis, D., Bush, A.M., Bozika, E., Tatsi, E., Simpson, A.E., Sweetman, R., 2004b. A novel method for removing phosphorus from agricultural runoff and sewage effluent. In: Lewis, D., Gairns, L. (Eds.) Agriculture and the Environment – Water Framework Directive and Agriculture, Proc. SAC and SEPA Biennial Conference, 24-25 March 2004, Edinburgh. Scottish Agricultural College and Scottish Environment Protection Agency, Edinburgh, UK, pp.174-180.

Heal, K.V., Dobbie, K.E., Bozika, E., McHaffie, H., Simpson, A.E., Smith, K.A., 2005. Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment. Water Sci. Technol. 51(9), 275-282.

Johansson Westholm, L., 2006. Substrates for phosphorus removal – Potential benefits for on-site wastewater treatment? Water Res. 40, 23-36.

Mainstone, C.P., Parr, W., 2002. Phosphorus in rivers – ecology and management. Sci. Total Environ. 282-283, 25-47.

Mayes, W.M., Potter, H.A., Jarvis, A.P., 2008. Novel approach to zinc removal from circum-neutral mine waters using pelletized recovered hydrous ferric oxide. J. Hazard. Mater. (in press)

Patrick Jr., W.H., Gotoh, S., Williams, B.G., 1973. Strengite dissolution in flooded soils and sediments. Science 179, 564-565.

Patrick Jr., W.H., Khalid, R.A., 1974. Phosphate release and sorption by soils and sediments: Effect of aerobic and anaerobic conditions. Science 186, 53-55.

Rorabacher, D.B., 1991. Statistical treatment for rejection of deviant values – critical values of Dixon Q parameter and related subrange ratios at the 95-percent confidence level. Anal. Chem. 63, 139-146.

SEPA, 2002. Technical Guidance Manual for Licensing Discharges to Water, Annex G (October 2004). http://www.sepa.org.uk/guidance/water/index.htm, accessed 06.05.08

Shilton, A.N., Elmetri, I., Drizo, A., Pratt, S., Haverkamp, R.G., Bilby, S.C., 2006. Phosphorus removal by an `active' slag filter – A decade of full scale experience. Water Res. 40, 113-118.

Sibrell, P., 2007. Method of Removing Phosphorus from Wastewater. U.S. Patent No.: US 7,294,275 B1.

Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. Mine Water Hydrology, Pollution, Remediation. Kluwer Academic Publishers, Dordrecht.

Table 1. P mass removal by the trough in the different phases of the experiment conducted at Leitholm WWTP. It is assumed that all P removal in trough is by ochre. Values outside brackets are for TP. Values within brackets are for SRP. Values are means ±95% CI for each phase.

Phase	P influx to trough (g P kg^{-1} ochre d^{-1})	P mass removal			% P mass removal
		(g P)	(g P kg^{-1} ochre)	(mg P kg^{-1} ochre d^{-1})	
2a	0.094±0.020 (0.082±0.021)	-4410±10900 (-3590±9360)	-2.1±5.2 (-1.7±4.4)	-18±44 (-14±38)	-19±-47 (-18±-46)
2b	0.15±0.035 (0.13±0.036)	25800±18900 (22300±19500)	24±9.0 (21±9.2)	65±48 (56±49)	45±35 (45±41)
3	0.29±0.039 (0.24±0.033)	2630±3370 (1280±1910)	5.2±1.6 (2.6±0.91)	46±59 (22±33)	16±20 (9±14)
4	0.024±0.004 (0.021±0.003)	388±181 (250±146)	0.77±0.09 (0.50±0.07)	13±6 (8±5)	54±27 (38±23)

Figure 1. Schematic diagram (not to scale) of the ochre-filled trough in the experiment to treat secondary-treated effluent at Leitholm WWTP.

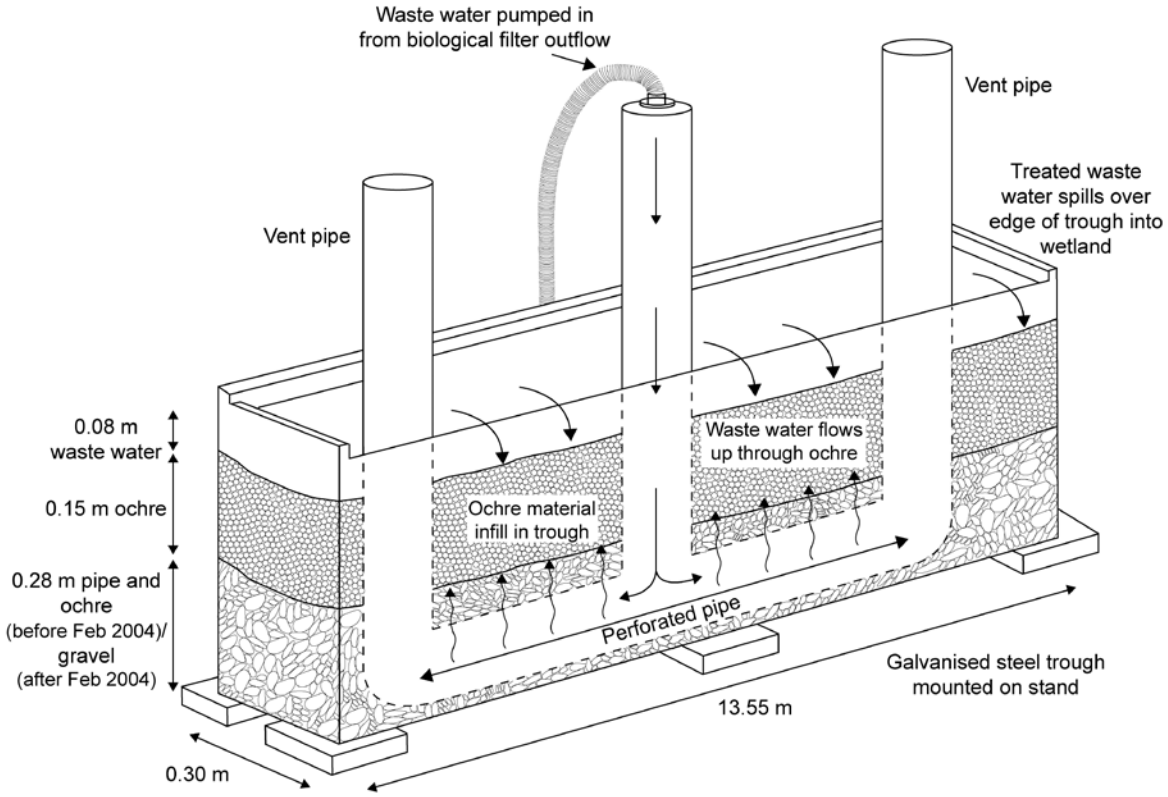
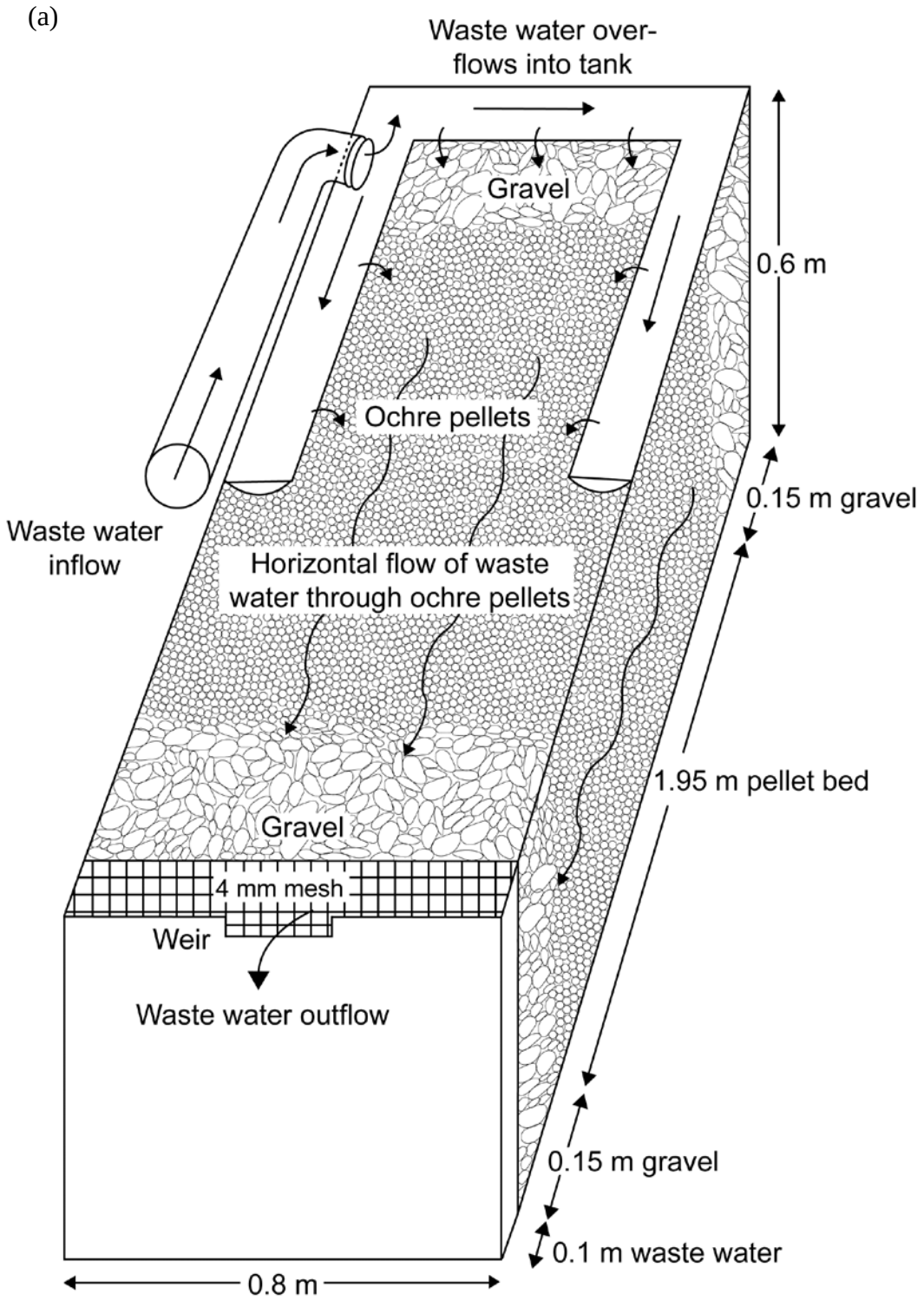


Figure 2. Schematic diagrams (not to scale) of the tank containing ochre pellets in the experiment to treat final effluent at Windlestone WWTP for (a) horizontal saturated flow conditions, and (b) vertical saturated flow conditions.



(b)

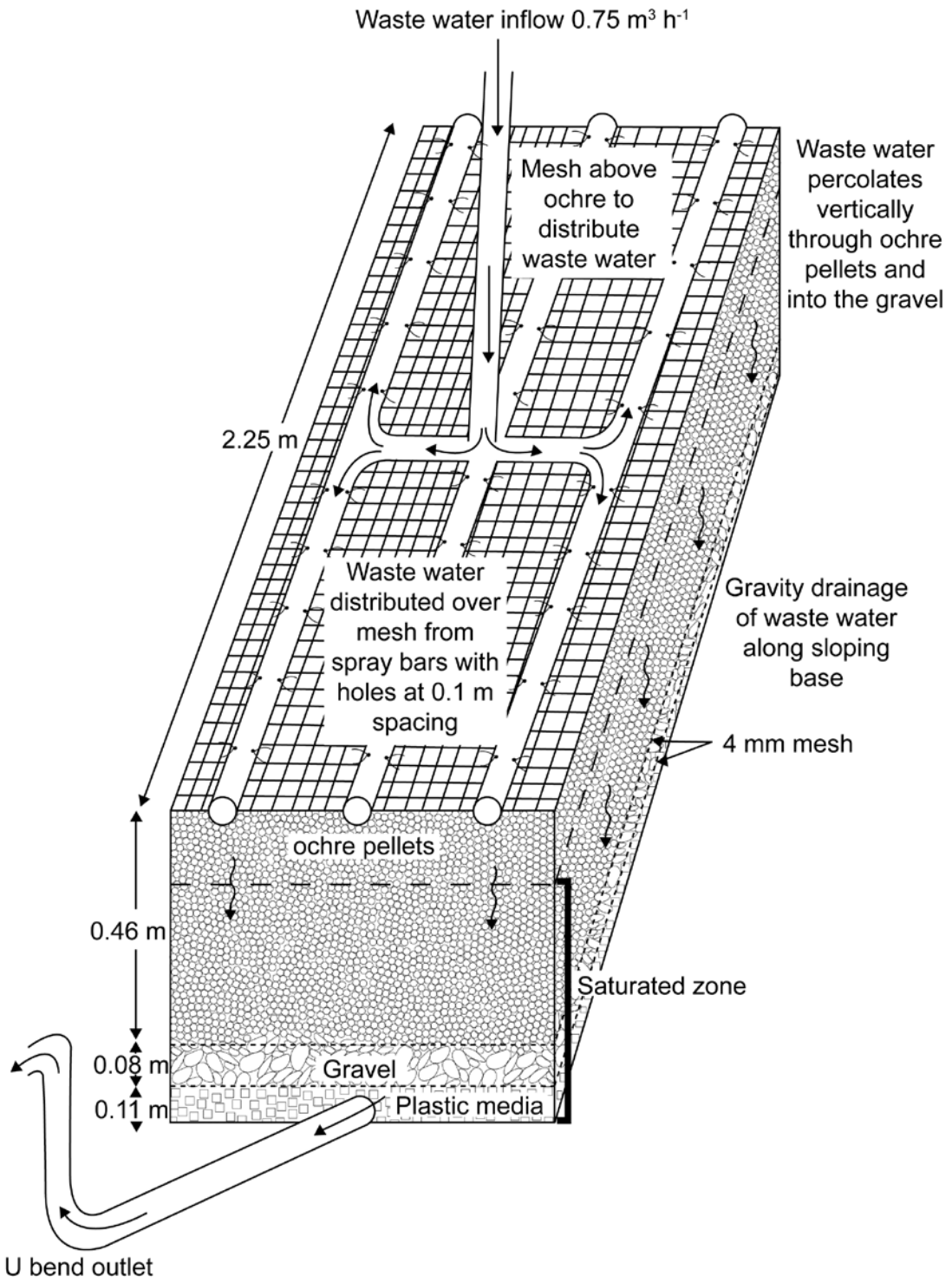

Waste water inflow 0.75 m³ h⁻¹
Mesh above ochre to distribute waste water
Waste water percolates vertically through ochre pellets and into the gravel
2.25 m
Waste water distributed over mesh from spray bars with holes at 0.1 m spacing
Gravity drainage of waste water along sloping base
4 mm mesh
ochre pellets
0.46 m
Saturated zone
0.08 m
Gravel
0.11 m
Plastic media
U bend outlet

Figure 3. (a) TP and (b) SRP concentrations (mean ± standard error) in filter outflow (also trough inflow in Phases 2-4), trough outflow and wetland outflow in different phases of the experiment at Leitholm WWTP. Letters/numbers above bars indicate significant differences within a phase.

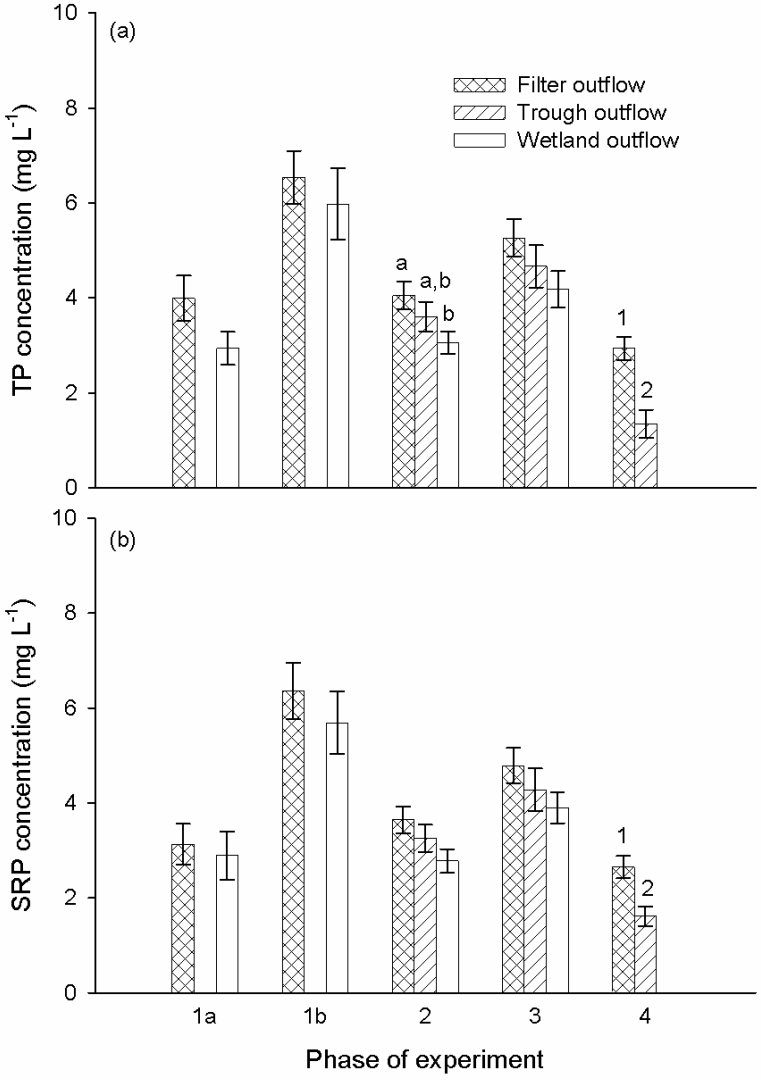


Figure 4. (a) % TP removal by concentration (mean ± standard error) by the wetland (wetland and trough after Phase 1) and ochre-filled trough alone in the different phases of the experiment at Leitholm WWTP. Numbers above bars indicate significant differences in TP removal by the trough between the phases of the experiment. (b) % TP removal by concentration in the trough containing ochre pellets before and after the inflow rate was restricted (i.e., in Phases 3 and 4 of the experiment at Leitholm WWTP). Values have been calculated for each effluent sampling occasion in Phases 3 and 4.